LETTERS TO THE EDITOR

On the Principle of Minimum Entropy Production

Dear Sir:

Because of frequent unqualified references to the Principle of Minimum Entropy Production (PMEP), quite often to bolster teleological arguments, I would like to call attention to a paper published several years ago in a symposium volume which is perhaps unknown to many biophysicists. In the course of trying to discover a general variational principle for steady-state dissipative systems, D. H. Gage et al. (1966) found that "unfortunately, this work leads instead to the establishment of a nonexistence theorem." They demonstrated the impossibility of finding a universal extremal functional of the form (in one dimension),

$$I = \int_{A}^{B} \Phi \left(L_{ij}, \phi_i, X_i = \frac{d\phi_i}{d\xi} \right) d\xi \tag{1}$$

where Φ is a specific function of its arguments, such that

$$\delta I = 0 \tag{2}$$

is equivalent to the steady-state conservation equation

$$\frac{dJ_i}{d\xi} = 0 \tag{3}$$

Standard notation is used; ξ denotes physical extent.

Given a more general notion of entropy, it might be possible to find a PMEP, but the preceding result precludes a PMEP based upon the usual definition of entropy. The well known PMEP of Prigogine (1961) is limited to systems which have constant coupling coefficients, L_{ij}. The nonexistence theorem of Gage et al. is powerful because it goes beyond entropy to state that there is absolutely no functional of all the arguments which would give a minimum principle for the steady state. A minimum principle would have to depend upon fewer and/or additional arguments. Nevertheless, in spite of the nonexistence of a general PMEP, we can discover several properties of dissipative systems of interest to the biophysicist.

MINIMUM ENTROPY PRODUCTION

We shall assume that the system is in a state of minimum entropy production. No assumptions are made concerning either the potential function, ϕ, or the Onsager coefficient, L. We consider a system with one flow. The variation of the total entropy production, P, is

$$\delta \int L(\nabla\phi)^2 \, dV = \int \left[\frac{\partial L}{\partial \phi} (\nabla\phi)^2 \, \delta\phi + 2L\nabla\phi\nabla(\delta\phi) \right] dV. \tag{4}$$

By the divergence theorem, we have

$$\int L\nabla\phi\nabla(\delta\phi)\ dV = \int (\delta\phi)L\nabla\phi\cdot\vec{n}\ dA - \int (\delta\phi)\nabla(L\nabla\phi)\ dV \qquad (5)$$

and, since all variations of the potential on the surface are zero, we have

$$\delta P = \int \left[\frac{\partial L}{\partial \phi} (\nabla\phi)^2 - 2\nabla(L\nabla\phi) \right] (\delta\phi)\ dV. \qquad (6)$$

We postulated that $\delta P = 0$ and so by the fundamental theorem of the calculus of variations, the associated Euler-Lagrange equation is

$$\nabla(L^{1/2}\nabla\phi) = 0 \qquad (7)$$

We therefore conclude that minimum entropy production does not necessarily imply steady state.

STEADY STATE

We shall assume that the system is in steady state and so is characterized by the equation

$$\nabla(L\nabla\phi) = 0 \qquad (8)$$

This equation differs from equation 7 by having L instead of $L^{1/2}$; therefore, if in the preceding section we had considered

$$\delta \int L^2(\nabla\phi)^2\ dV = 0 \qquad (9)$$

then the resulting Euler-Lagrange equation would have been equation 8. We conclude that equation 9 is the variational principle implied by steady state; the variation can also be expressed

$$\delta \int J^2\ dV = 0 \qquad (10)$$

MINIMUM ENTROPY PRODUCTION AND STEADY STATE

If one agrees with the contention of the steady-state existence of biological organisms and also wishes to believe in an intrinsic metabolic efficiency resulting from a minimum dissipation of entropy, then what conditions does this impose upon the organism's relationship to its environment?

With a simple vector identity, we can write the variation of the total entropy production as

$$\delta P = \delta \int \nabla(L\phi)\nabla\phi\ dV - \delta \int \phi\nabla L\nabla\phi\ dV \qquad (11)$$

If we multiply the equation of steady state by ϕ and expand, we obtain

$$\phi \nabla L \nabla \phi = -\phi L \nabla^2 \phi \qquad (12)$$

which is the last term in equation 11. By Green's first identity, equation 11 then becomes

$$\delta P = \int \left[(\delta\phi) L \nabla \phi + \phi \delta(L \nabla \phi) \right] \cdot \vec{n} \, dA \qquad (13)$$

We assumed that $\delta P = 0$. Also the preceding variation is subject to the steady-state constraint that the integral of the normal component of the flow across the surface is zero. The organism must somehow be able to react to changes in the external environment in a manner which makes the surface integral in equation 13 equal to zero. To do this globally would require an elaborate central control system. However, if the organism retained its minimum dissipation and its steady state by reacting locally to changes at its surface, then at any surface element

$$\delta\vec{J} = -\frac{\delta\phi}{\lambda-\phi} \vec{J}. \qquad (14)$$

where λ is a Lagrangian multiplier.

In other words, a surface element of an organism initially faces an external environment characterized by the value ϕ for the state variable and has a steady flow, $\vec{J}$, through it. These two functions, of course, can be functions of the space variables. If the external state variable changes locally by $\delta\phi$ then the response of the organism is to change the flow by $\delta\vec{J}$ a given by equation 14. Such a change insures steady-state and minimum dissipation in the new altered environment.

REFERENCES

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I. W. RICHARDSON
Institute of Physiology
Aarhus University
Aarhus, Denmark